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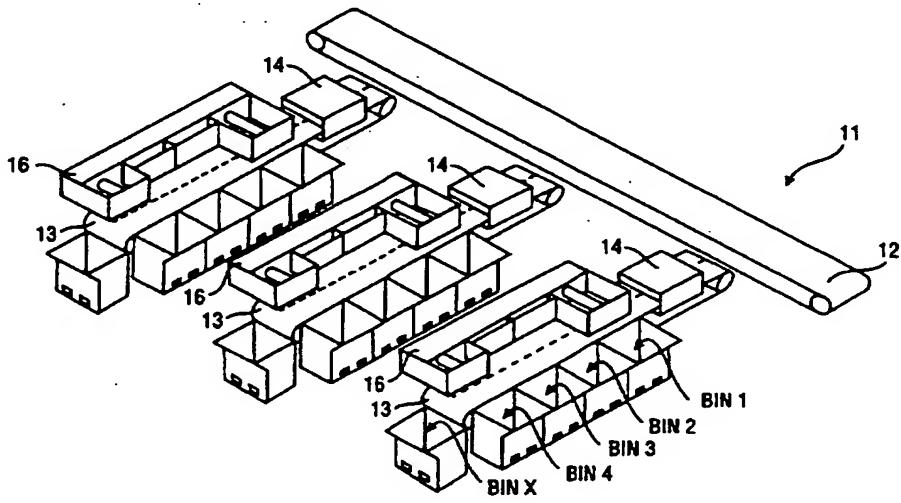
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(54) Title: GLASS COMPOSITION DETERMINATION METHOD AND APPARATUS



(57) Abstract

A method and apparatus for determining the composition of glass, and for sorting glass according to composition. Glass of unknown composition is irradiated and an x-ray fluorescence spectrum is detected from the glass. The detected x-ray fluorescence spectrum is then compared with a plurality of fluorescence spectra corresponding to glasses of known composition. The glass of unknown composition is then determined to correspond in composition to the glass of known composition having an x-ray fluorescence spectrum most closely matching the spectrum detected from the glass of unknown composition. The glass may then be sorted according to determined composition. In operation, a substantially continuous stream of glass pieces is irradiated by x-ray instruments (14) and detected while the stream is moving on conveyors (13). Once the composition of a piece of glass in the stream is determined, it is diverted into an appropriate container of like compositioned glass by rams (16).

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DESCRIPTION**GLASS COMPOSITION DETERMINATION METHOD AND APPARATUS**BACKGROUND OF THE INVENTION

5 The invention relates to a method and apparatus for determining the composition of glass of unknown composition, and for sorting glass according to composition.

10 The environmental regulations of the U.S. and other nations currently classify the glass and other components of television tubes and color computer monitors as hazardous waste. Due to this classification, the direct landfilling of tubes which are found to be defective or which are broken in manufacturing, is no longer permitted. The disposal of this material requires a stabilization treatment before it can be legally landfilled. Elsewhere in the world there are more
15 stringent restrictions on the disposal of these materials.

20 To further complicate the disposal issue, discussions have been started at various regulatory agencies concerning the disposal of cathode ray tubes (CRTs) from television sets and color computer monitors at the end of their useful life.
25 There are approximately 250,000,000 television sets and 60,000,000 computer monitors in use in the United States. The disposal of 5% of the television sets and 10% of the computer monitors would represent an estimated 130,000 tons of CRT glass annually. Landfill disposal is the least desirable option for both the generator and the municipal planners.

30 The environmental issue which is of most concern relative to the disposal of the CRT glass is the potential for lead to be released from the materials. The most vulnerable portion of the CRT tube is the frit which is used to join the face plate (panel) to the funnel. This frit is comprised largely of lead oxide, which is slightly soluble in weak acids and thus vulnerable to leaching and migration into ground waters when buried in a landfill.

- 2 -

The CRT glass contains substantial quantities of lead oxide (PbO). Generally, lead oxide in this form is inert and environmentally stable. If the lead bearing glass is broken up or ground up into a fine powder and exposed to an acidic environment, such as might exist in a landfill, small quantities of lead can 5 be leached out.

In addition, the interior coatings of older television CRTs contain high levels of cadmium compounds which are toxic. The landfilling of these CRTs can lead to the leaching of the cadmium compounds and their release into the ground 10 water. The current manufacturing processes utilize different coatings which are not known to be toxic or carcinogenic; however, toxicological studies are being performed on a continuous bases to insure the safety of those who come in contact with the materials.

15 A perception exists that large amounts of lead would potentially be disposed of by the landfilling of electronic assemblies. It is therefore desirable to avoid landfilling these materials in order to lower costs, reduce the environmental risk and to assure the public safety.

20 The avoidance of landfill disposal should preferably encompass the total use of the glassy materials of the television CRTs, defective tubes and debris from manufacturing. Much of the current practice involves the reformulation of these glasses into raw materials. The raw materials are then used to make new products including electrical resistance glass; decorative glass; glass for the absorption of 25 low-level radiation from low-level radioactive wastes; glass for retroreflective use and high density glass. In these cases, the products are unique in their function or in their substitution for other glasses. In all cases, the products have greater value in use or are lower priced substitutes for existing products manufactured from non-recycled glass. A competitive advantage exists in the use of waste streams as raw 30 materials for the manufacture of these unique products.

- 3 -

While the reformulation of CRT derived cullet into some new products does not require careful control of cullet formulation, if the glasses could be successfully separated by formulation from waste stream, then they would be more easily reformulated into useful products. By identifying the glass composition, it 5 would be easier to channel cullet to the appropriate process for inclusion as a raw material in the production of a final salable product.

In addition to the utilization of the separated glasses as raw materials in the manufacture of secondary products, a new market has been established for the 10 resale of the identified glass back to the CRT manufacturers for remelting. The criteria for this type of separation and recycling are very stringent and the separation requires highly accurate identification of the glass composition. CRT glass is a high quality optical glass. In order to manufacture this glass to the required quality standards, it is necessary to insure that the composition remain 15 stable. The use of clean cullet is desirable because it allows the generator to avoid the cost of landfilling and reduces the melting costs. The remelting of cullet requires significantly less energy than melting raw materials to form the same glass. Compositional upsets can occur if the cullet is misidentified. This situation can result in large monetary losses on the order of \$300/ton plus the cost of any 20 processing.

The key component to the successful use of the discarded glass is accurate and reliable sorting. If the sorting is done accurately, the glass plant can save as much as \$170/ton for materials and processing. In addition, in order to be 25 commercially viable, sorting should be fast.

It would therefore be desirable to provide a means for accurately, reliably and quickly sorting CRT derived glass cullet according to glass composition.

- 4 -

SUMMARY OF THE INVENTION

The present invention satisfies the above-noted requirements by providing a method and apparatus for determining the composition of glass of unknown 5 composition using x-ray fluorescence spectroscopy, and for sorting glass according to composition.

More particularly, the present invention uses x-ray fluorescence spectroscopy for identification of the key constituents of glass cullet. This process 10 involves the exposure of a piece of glass to an x-ray source. The interaction of the x-rays with the elements of the glass results in a fluorescence emission spectrum of radiation which is characteristic of each element present in the cullet. The intensities of the fluorescence emission spectrum peaks are dependent on the 15 quantity of the elements present. By measuring the intensities of the emission fluorescence peaks, a quantitative determination of the elements present may be made.

The invention also includes a conveyor system for the presentation of the glass cullet to the x-ray system. The design results in the accurate placement of 20 the glass thus enabling the x-ray fluorescence spectra to be acquired while permitting the efficient movement of the glass through the process.

Another feature of the invention is the utilization of x-ray fluorescence analysis as an input to a mechanical sorting system. The mechanical sorting 25 system operates to separate the glass cullet by composition. The integration of the analysis results with the mechanical sort may be completed using various computers, programmable logic controllers and software. These devices provide the appropriate signals to the mechanical sorting devices.

- 5 -

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an isometric view of an exemplary apparatus in accordance with the present invention.

5

Figure 2 is a more detailed illustration of a portion of glass sorting apparatus of Figure 1.

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Figure 3 is a block diagram of the glass sorting apparatus of Figure 3.

Figure 4 is a block diagram of another embodiment of the glass sorting apparatus in accordance with the present invention.

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Figure 5 is a flow chart of the glass sorting method of the present invention.

Figure 6 is a flow chart of the sample processing method of the present invention.

20

Figure 7 is an exemplary flow chart of library searching methods, in accordance with the present invention.

Figures 8 is a block diagram of a tree-based library searching method, in accordance with the present invention.

25

Figures 9, 10 and 11 are exemplary x-ray intensity spectra, illustrating various features of the present invention.

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- 6 -

DETAILED DESCRIPTION

Referring to Figure 1, presented in an exemplary glass sorting apparatus 11, in accordance with the present invention. In the illustrated embodiment, 5 apparatus 11 includes three, substantially identical, glass sorting stations, each fed by common input conveyor 12. Each station includes sortation conveyor 13, which conveys glass from input conveyor 12, x-ray instrument 14, ram or pusher assemblies 16, and a number of cullet receiving bins (bin 1, bin 2, bin 3, bin 4 and bin x). As explained below in more detail, in operation, glass cullet is 10 conveyed along input conveyor 12, and on to a sortation conveyor 13. Conveyor 13 then conveys the cullet through x-ray instrument 14, which, in accordance with the present invention, determines the composition of the cullet using x-ray fluorescence spectroscopy. Then, as the identified cullet continues to be conveyed along sortation conveyor 13, an appropriate ram is activated to push the cullet into 15 an appropriate bin, or if no ram is activated, to permit the cullet to fall into bin x at the end of sortation conveyor 13.

It should be noted that although three glass sorting stations are illustrated in Figure 1, one or more stations may be used without departing from the scope of 20 the invention. In addition, although each station illustrated in Figure 1 is fitted with five bins, it will be understood that any number of bins may be used.

Referring now to Figure 2, presented in more detail is one of the glass sorting stations illustrated in Figure 1. A piece of glass 24, of unknown 25 composition, is moved by sortation conveyor 13 and passes over an x-ray fluorescence spectroscopy head 20 including x-ray source 21 and x-ray detector 22. In an exemplary embodiment of the present invention, x-ray source 21 is a 60 keV, 30 milliCurie, americium (^{241}Am) radiation source available from Amersham, Corp., and x-ray detector 22 is a two atmosphere argon detector, model No. 30 45129, available from LND, Inc.; however, other radiation sources and detectors may also be used. As glass 24 moves over the x-ray fluorescence spectroscopy head 20, x-rays 23 emitted from x-ray source 21 are directed to glass 24, and

- 7 -

detector 22 detects both x-rays that are scattered from glass 24, as well as x-ray fluorescence emitted by glass 24. X-ray source 21 preferably is fitted with a collimator (not shown).

5 As glass 24 moves over the x-ray fluorescence spectroscopy head 20, the x-ray signal produced by detector 22 increases, and as glass 24 moves away from head 20, the x-ray signal produced by detector 22 decreases, thus permitting the detection of the presence or absence of glass over head 20, based upon the x-ray spectrum alone, without requiring additional detecting devices.

10

As explained below in more detail, the x-ray spectrum produced by detector 22 is characteristic of the various constituent components present in glass 24.

15

In accordance with one embodiment of the present invention, measurements are taken by detector 22 approximately 16 times per second in order to be able to detect edges of glass 24. On average, in accordance with the exemplary embodiment, glass 24 spends approximately one second over x-ray head 20. Other sampling and dwell times would also be acceptable.

20

Referring now to Figure 3, presented is a block diagram of the signal processing components of the invention. The output of x-ray detector 22 is an analog signal appearing on line 31, which is applied to multi-channel analyzer (MCA) 32, which produces on line 33, digitized x-ray spectra (illustrated, for example, in Figures 9-11), for presentation to computer 34. An exemplary multi-channel analyzer usable for this purpose is commercially available from Asoma Instruments, of Austin, Texas.

25

30

Computer 34 analyzes the x-ray spectra applied on line 33 to determine the composition of the glass represented by the applied spectra. Then, computer 34 sends a signal to one of rams 16 (see also Figures 1 and 2) at the appropriate time to push the piece of glass that was analyzed into the appropriate bin. More than

- 8 -

one piece of glass may be on the output conveyor simultaneously. Computer 34 schedules the activation of rams 16 to coincide with the eventual presence of the analyzed glass near the desired bin.

5 Figure 4 presents in block diagram form an alternate embodiment of the present invention, which includes three stations, each having a dedicated multi-channel analyzer 41, which are connected to a single computer 42. Computer 42, in turn, is connected to programmable logic controller 43 (for example, available from Allen Bradley), which in turn controls the rams 16 of all stations of the
10 apparatus to push the sorted glass pieces into the appropriate bins after glass composition has been determined.

Referring now to Figures 5-7, presented in flow chart form is the glass sorting method of the present invention. In practice, the method illustrated in the
15 flow charts of Figures 5-7 is encoded in appropriate form and loaded into computer 34 or 42, in order to cause the apparatus illustrated in Figures 1-4 to perform the method of the present invention.

Referring to Figure 5, operation block 51 and decision block 52 are
20 configured in a loop to cause detector 22 (see also Figure 2), to detect x-ray fluorescence and scattered x-rays. If decision block 52 detects that the x-ray intensity is greater than a predetermined threshold, it is concluded that a piece of glass is present over head 20, and control passes to block 53. Operation block 53 and decision block 54 are also configured in a loop to cause detector 22 to detect
25 x-ray fluorescence and x-rays scattered from glass 24, while glass 24 is over head 20. During the loop, the samples are stored by block 56. If it is determined that the detected x-ray intensity has fallen below a predetermined threshold (indicating that glass 24 is leaving head 20), control passes to block 57 where the samples collected in block 56 are analyzed. This analysis is presented below in more detail
30 with reference to Figure 6.

- 9 -

Control then passes to block 58 where it is determined whether the analysis performed in block 57 has resulted in the accurate identification of the composition of glass 24. If so, control passes to block 59, wherein a particular bin for the glass is determined and the corresponding ram is scheduled to be activated at the 5 appropriate time to eject the glass 24 into the appropriate bin. After the scheduling of what to do with the glass is done by block 59, control turns to block 51 where the next piece of glass of unknown composition is analyzed.

The scheduling of future ramming is important to system throughput.
10 Block 57, 58 and 59 should execute in less time than it takes conveyor 13 to present the next piece of glass, at least on the average.

The present invention thus presents a reliable, accurate, continuously operating glass sorting method and apparatus, which permits precision, automated 15 glass sortation according to composition, resulting in commercially viable glass sortation.

Referring now to Figure 6, presented in more detail is the sample processing method of step 57 of Figure 5. Beginning in step 61, analysis has 20 begun at the center of the data stored in block 56 (Figure 5), ensuring that analysis has begun using data corresponding to the center of glass 24. Control then passes to block 62 where the data is corrected for the curvature of the glass. This is accomplished through a normalization procedure that produces normalized spectrum by dividing individual raw intensities, by the sum of the raw intensities 25 at selected energies. Normalization of the raw x-ray intensity is necessary in order to correct for sample curvature and possible other sample presentation errors such as height above x-ray head and for the variable time each sample actually spent. In the present invention each of the raw x-ray intensities are divided by their sum. The resultant normalized values then sum to one.

30

For example, if the counts for Pb, Sr, Zr and Ba are 100, 200, 300 and 400, respectively, then the normalized counts are: $100/(100+200+300+400)$,

- 10 -

$200/(100+200+300+400)$, $300/(100+200+300+400)$ and
 $400/(100+200+300+400)$, respectively. These ratios are: 0.1, 0.2, 0.3 and 0.4,
respectively.

5 After normalization, control passes to block 63 where the corrected counts
and total counts are accumulated. Then, in decision block 64, it is determined
whether the portion of the spectrum corresponding to lead content of the glass
indicates that the lead content of the glass is on the correct side of a predetermined
threshold. "Correct side" means that if leaded glasses are to be sorted out, then
10 the measured lead must be above the threshold; if unleaded glasses are to be sorted
out, than it must be lower. This is done as a separate step as this determination
can be reliable even if the match cannot be. This allows an otherwise identified
glass to be sorted into leaded and unleaded "waste." The importance of this is that
lead is a serious containment for unleaded glass processes. Some amount of
15 unclassified unleaded glass may be mixed in with properly identified leaded glass
with little consequence to further processing; however, if leaded glass mixes in
with properly identified unleaded glass, a whole batch can be spoiled.

If glass 24 is concluded to include lead, control is returned to block 58 of
20 Figure 5, with an indication that the glass sample includes lead. If, on the other
hand, decision block 64 determines that lead is not present in the glass sample,
control passes to decision block 66 where the total number of counts is assessed.
If the total number of counts is less than a predetermined number, thus indicating
that the glass sample is too small for accurate composition determination, control
25 passes to decision block 67 where it is determined whether additional data is
available for analysis. If not, control is returned to decision block 58 of Figure 5
indicating that no match for the glass under consideration can be determined. If,
on the other hand, decision block 67 determines that additional data is available
for analysis, control is returned to block 62.

30

If decision block 66 determines that the total count is above the
predetermined threshold, control passes to block 68 where the composition of the

- 11 -

glass is determined, in accordance with the method presented in more detail with reference to Figure 7.

Control then passes to block 69 where it is determined whether block 68
5 has found that the glass under consideration matches the spectrum of a glass of known composition. If it does not, control passes to block 71 where the match counter is cleared, and control returns to block 62.

The match counting is a statistical hedge against making errors. Adding
10 data together then comparing the sum has a different error rate than comparing subsets of data to see if all the comparisons agree. The goal of match counting is to use the least amount of data that gives a reliable answer.

If decision block 69 determines that there is a match, control passes to
15 block 70 where the match counter is incremented. Control then passes to block 72 where it is determined whether the match counter has reached a predetermined number, and if so, the occurrence of the match is concluded, and control is returned to block 57 of Figure 5. If, on the other hand, decision block 72 determines that the match counter criteria has not been met, control is returned to
20 block 62.

Referring now to Figure 7, the details of the glass composition analysis of step 68 are presented. In accordance with the present invention, the detected x-ray spectrum of scattered and fluorescence radiation from glass of unknown
25 composition, is compared to a library of a plurality of spectra of glasses of known spectral composition. In practice, glasses of known composition are placed on x-ray head 20 (see also Figure 2), and the spectrum detected by detector 22 is recorded in a library. The same procedure is performed for other glasses of known composition. The individual spectra are stored in the form of normalized
30 spectral intensity peaks at predetermined energy levels corresponding to elements contained within the glasses. Elements in typical CRT glass, most of which exhibit clearly definable x-ray fluorescence peaks at specific energy levels,

- 12 -

include: silicon (Si), aluminum (Al), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), lead (Pb), zirconium (Zr), zinc (Zn), sodium (Na), potassium (K), titanium (Ti), cerium (Ce), antimony (Sb), arsenic (As), fluorine (F), and iron (Fe).

5

In accordance with the present invention, intensities of the fluorescence spectra at spectral energy levels corresponding to a selected subset of these possible constituent components of CRT glass are selected for inclusion in the library, and are used for comparison against spectra derived from glasses of 10 unknown composition.

15

For example, in accordance with one embodiment of the present invention, it has been determined that fluorescence intensities for strontium, barium, lead and zirconium are sufficient to permit accurate and reliable discrimination between five known CRT glass compositions. While intensities at these four energy levels have proven sufficient to discriminate between these five known glass compositions, it should be understood that intensities at more or fewer energy levels may be used, without departing from the scope of the present invention.

20

Referring now to Figure 7, presented are two methods of comparing the spectrum from the unknown sample of glass, with the stored library of spectra of known glass compositions, to determine which, if any, matches the spectrum from the unknown sample.

25

In block 73, it is determined which method is desired, the "distance method" or the "tree method". If the distance method is desired, control passes to block 74 where certain parameters used in the method are initialized. Then, in block 76, the first library entry is selected. Each entry in the library includes the type (manufacturer) of glass, the bin into which it should ultimately be sorted, and 30 a list of the normalized x-ray intensities for each of the elements of interest, and possibly the scattered x-ray intensity.

- 13 -

Regardless of which sorting method is used, a figure of merit value is calculated. Should the figure of merit value exceed some predetermined threshold value, the accuracy of the identification is determined to be questionable, and the glass under consideration is tagged as unidentified rather than running the risk of

5 an incorrect identification. By making the threshold (or thresholds) for a match figure of merit lower, then the certainty of the identification is increased; however, more glass will end up being unidentified. On the other hand, by making the threshold for a match figure of merit higher, more glass will be identified and sorted into some bin, rather than going into the unidentified bin (bin

10 x). At the same time, the percentage of glass that is incorrectly identified increases.

The first matching method is termed the "distance" method, and begins with block 74 wherein certain parameters are initialized. Then, in block 76, the

15 first library entry is selected, and control passes to block 77 where a figure of merit for that entry is calculated. The figure of merit is based on the square root of the sum of the squares of the differences of the x-ray intensities for each of the characteristic x-ray intensities stored in a library. In two dimensions, this is simply the distance between the unknown and each of the library samples.

20

As an example, assume the following library entries exist, each including sample identification followed by four normalized x-ray intensities:

	<u>Sample Name</u>	<u>Intensity 1</u>	<u>Intensity 2</u>	<u>Intensity 3</u>	<u>Intensity 4</u>
25	A	0.1	0.2	0.3	0.4
	B	0.2	0.2	0.3	0.3
30	C	0.25	0.25	0.25	0.25

also assume the following spectrum for the unknown:

- 14 -

<u>Sample Name</u>	<u>Intensity 1</u>	<u>Intensity 2</u>	<u>Intensity 3</u>	<u>Intensity 4</u>
Unknown	0.22	0.18	0.31	0.29

5

The distance from the unknown sample to each of the library entries is calculated by taking the square root of the sum of the squares of the differences between the unknown's normalized x-ray intensities and each of the standards.

10

A spreadsheet showing the "figure of merit" for each of the samples follows:

15

	Intensity 1	Intensity 2	Intensity 3	Intensity 4	
Unknown	0.22	0.18	0.31	0.29	
					Figure of Merit
A	0.1	0.2	0.3	0.4	0.16
B	0.2	0.2	0.3	0.3	0.03
C	0.25	0.25	0.25	0.25	0.10

20

In this example, library entry B has the smallest figure of merit and is the best match to the unknown sample.

25

In block 78, the calculated figure of merit is compared against the best existing figure of merit. If the calculated figure of merit is less than the then existing best figure of merit, the present library entry under consideration is determined to be the closest match, so far, to the spectrum of the unknown sample, and control passes to block 79 where the presently calculated figure of merit replaces the best figure of merit, and the present library entry under consideration is stored as the best match (block 79). Control then passes to block 81 where the library pointer index is incremented to the next entry. In decision block 82, it is determined whether all entries in the library have been assessed. If

- 15 -

not, control returns to block 77, and if so, control passes to block 83 where the lowest calculated figure of merit is compared to a predetermined threshold to determine whether or not the best calculated figure of merit is sufficiently low to conclude that an accurate match has occurred. If so, the composition of the

- 5 library entry corresponding most closely to the unknown sample is concluded to be the composition of the unknown sample, and control returns to block 68 of Figure 6. If, on the other hand, decision block 83 determines that the best calculated figure of merit is not small enough, it is concluded that no match has occurred, and this information is returned to block 68.

10

Another search method is termed the "tree" sorting method, and uses the spectral intensities from each of the elements of interest individually, and makes decisions based upon predetermined threshold values. At each step along the tree, the list of possible identification is narrowed. At the end of each branch of the 15 decision tree is a "leaf" that corresponds to a particular library entry that most closely matches the unknown sample.

- In particular, beginning in block 84, the tree pointer (TREEPTR) is set to root. Then, in block 86 it is determined whether the tree pointer points to a null, 20 if so, no match is concluded and control is returned to block 68. If, on other hand, the tree pointer is not pointing to a null, control passes to block 87 where the threshold for the node is determined. Then, in block 88, the intensity of the particular element in the unknown sample is compared against the threshold. Depending upon this comparison, branching is accomplished according to steps 89 25 and 91. Control then passes to block 92 where it is determined whether the tree pointer is on a leaf of a decision tree. If not, control returns to block 86 where the next element intensity from the unknown sample is analyzed, using the threshold from the next node.

- 30 If decision block 92 determines that the tree pointer is on a leaf of the decision tree, control passes to block 93 where the particular library entry determined by the decision tree is selected, a figure of merit is calculated using the

- 16 -

spectrum selected from the library and the unknown spectrum, using the distance method described above with reference to steps 74 through 82. Then, as before, control passes to block 83 where it is determined whether the calculated figure of merit is small enough so that an accurate match can be concluded. Then control 5 returns to block 68 of Figure 6.

Referring now to Figure 8, presented is a diagrammatic view of the tree search method presented in flow chart form in steps 84 through 93 of Figure 7. Referring to Figure 8, an x-ray spectrum for glass of unknown composition (block 10 95), is applied to the primary search criteria of block 96. This search compares the intensity of a single energy of the fluorescence spectrum (indicative of a single glass component), with a predetermined threshold. For example, if lead exists in the glasses under consideration, the intensity of the unknown spectrum existing at 10.549 keV is compared with a predetermined threshold to determine whether or 15 not lead is present in the glass.

If the primary search criteria in step 96 is not satisfied, control passes to step 97 where secondary search criteria is applied. Similar to the primary search conducted in block 96, the secondary search in block 97 compares the intensity of 20 the fluorescence spectrum of the unknown glass at a particular energy level, which is indicative of a glass component, typically different from the glass component that was the subject of the primary search in block 96. For example, if the primary search is concerned with lead, secondary search 97 may be concerned with strontium.

25

In the example of Figure 8, after the secondary search is conducted in block 97, the unknown glass is identifiable as having a composition corresponding to that of either product E or product F. If the figure of merit calculation (performed in step 93 of Figure 7), indicates that the figure of merit calculated for 30 the spectrum of unknown intensity is too high, then it is concluded that the composition of the unknown glass cannot be identified (step 101).

- 17 -

- If the primary search 96 determines that the intensity of the spectrum at the particular energy level is greater than the predetermined threshold, control passes to block 102 where a secondary search is performed by comparing the intensity of the fluorescence spectrum at an energy level different from the energy level tested in the primary search, block 96, and that intensity is compared against a predetermined threshold.

- In the example given, depending on the results of the secondary search conducted in block 102, the unknown glass is concluded to correspond in composition to product A (block 103), or a tertiary search is conducted in block 104.

- As with the other searches, the tertiary search conducted in block 104 compares the intensity of the unknown spectrum at a third energy level, indicative of a third glass component, usually different from the glass components under consideration in the primary and secondary searches of steps 96 and 102. If the same element is under consideration, than the threshold is different. For example, a first search could split into low and high lead, then a second search could split the high lead into high and very high lead. The intensity of the unknown glass at that energy level is compared with a threshold, and the results indicate that the unknown glass corresponds to the composition of product B (block 106), or that the quartenary search of block 107 should be conducted.

- As with the other search nodes, the quartenary search conducted in block 107 compares the intensity of the spectrum of the glass of unknown composition at a fourth energy level, with a predetermined threshold. In the example illustrated, the results of quartenary search 107 indicate that the glass of unknown composition corresponds to the composition of product C (block 108), correspond to the composition of product D (block 109), or if the calculated figure of merit is too high, that the unknown glass cannot be identified (block 110).

- 18 -

It should be apparent from the description of the tree sorting method described with reference to blocks 84 through 93 of Figure 7 and Figure 8, that the tree may be tuned by adjusting the thresholds used at each node, and by testing for the presence of different glass components (indicated by different energy levels), at each node. In addition, the number of search nodes is variable, and will depend upon the number of possible known glass compositions that are being considered.

Referring now to Figure 9, presented in graphical form are the fluorescence spectra of two products (product A and product B), superimposed upon one another. As can be seen, the two spectra indicate that the two glasses are nearly identical in composition, with only small differences in the quantity of strontium (14.142 keV) existing between the two samples. The levels of Pb (10.549 keV), Zr (15.746 keV), and Ba (32.066 keV), being virtually identical for the two samples. The cadmium peak (23.109 keV) is due to the cadmium collimator used with the x-ray source 21 (Figure 2), and is not used in the determination of glass composition. Backscatter is also present at approximately the energy level of the x-ray source.

Figure 10 presents a magnified view of the Sr spectral region of the spectra of Figure 9, indicating that the two spectra differ in intensity by approximately 1,000 units in this region. In accordance with the present invention, the library entries for products A and B would include the intensity of Sr, and the difference in intensities will permit the correct characterization of glass of unknown composition, as corresponding to either product A or B, using the methods described above.

Referring to Figure 11, presented are two additional fluorescence spectra for products C and D of known composition. As can be seen, these two products correspond in the quantity of Sr, but differ greatly in the quantities of Pb and Ba. The large difference in the Ba content between products C and D indicate that Ba (32.066 keV), would be a useful energy level of the fluorescence spectrum to

- 19 -

discriminate between products C and D for one of the nodes of the tree search method illustrated in steps 84 through 93 of Figure 7 and illustrated in Figure 8.

It will be understood that although the present invention has been described
5 with reference to particular embodiments, additions, deletions and changes could
be made to these embodiments, without departing from the scope of the present
invention.

- 20 -

CLAIMS

1. A method of determining a composition of at least one glass piece of a substantially continuous series of glass pieces of unknown composition,
5 comprising:
irradiating said glass piece of unknown composition with x-rays;
detecting an x-ray fluorescence spectrum emanating from said glass piece
of unknown composition;
automatically comparing said detected spectrum with each of a plurality of
10 predetermined x-ray fluorescence spectra, each corresponding to
glass of known composition; and
determining a composition of said glass piece of unknown composition as a
function of said comparison.
- 15 2. The method of claim 1, said irradiating step comprising:
conveying said glass piece while irradiating said glass piece.
3. The method of claim 1, said detecting step comprising:
conveying said glass piece while detecting said x-ray fluorescence spectrum
20 emanating from said glass piece.
4. The method of claim 1, further comprising:
normalizing said detected spectra to adjust for varying geometry of said
series of glass pieces.
- 25 5. The method of claim 4, said normalizing step comprising:
dividing intensities of said detected spectrum occurring at each of a
plurality of selected energy levels within said spectrum, by a sum of
said intensities, to produce a normalized intensity at each of said
plurality of energy levels.

- 21 -

6. The method of claim 5, further comprising:
selecting said plurality of energy levels to correspond to fluorescence peaks
of elemental components of glass.
- 5
7. The method of claim 1, said detecting step comprising:
determining the presence or absence of a piece of glass as a function of
said detected spectrum.
- 10 8. The method of claim 1, further comprising:
 - a. a radiating glass of known composition;
 - b. detecting a fluorescence spectrum from said glass of known
composition;
 - c. determining a plurality of intensities of said fluorescence spectrum
at energy levels corresponding to predetermined glass components;
 - d. storing said plurality of intensities as one of said plurality of
predetermined x-ray fluorescence spectra; and
repeating each of steps a-d for other glass of known composition.
- 15
20 9. The method of claim 8, said comparing step comprising:
automatically comparing intensities of said detected spectrum of said glass
of unknown composition at said energy levels corresponding to said
predetermined glass components, with respective intensities in each
of said predetermined x-ray fluorescence spectra.
- 25
30 10. The method of claim 9, said step of determining composition of said glass
of unknown composition comprising:
calculating a figure of merit for each of said plurality of predetermined x-
ray fluorescence spectra by calculating the square root of the sum of
the squares of the differences of the intensities of said detected
spectrum of glass of unknown composition and the respective
intensities in said predetermined x-ray fluorescence spectra; and

- 22 -

determining that said glass of unknown composition corresponds to the composition of the glass with the predetermined x-ray fluorescence spectrum having a minimum figure of merit.

- 5 11. The method of claim 1, further comprising:
 sorting said glass of unknown composition according to determined
 composition.
- 10 12. The method of claim 1, said step of automatically comparing comprising:
 determining intensities of said detected spectrum at predetermined energy
 levels; and
 subjecting said determined intensities to a tree-sorting method.
- 15 13. A glass cullet processing apparatus, comprising:
 an x-ray source and an x-ray fluorescence detector, each located adjacent a
 glass testing position;
 means for conveying glass cullet to and from said glass testing position;
 and
 data processing means, connected to said detector and including a stored
20 library of x-ray fluorescence spectra of glass of known composition,
 for comparing an x-ray fluorescence spectrum obtained from glass
 cullet in said glass testing position with each spectra in said library,
 and for providing an indication of glass cullet composition as a
 function of the comparison.
- 25 14. The apparatus of claim 13, further comprising:
 means, responsive to said indication of glass cullet composition, for
 diverting said glass cullet from said means for conveying into one of
 a plurality of containers.

30

1/15

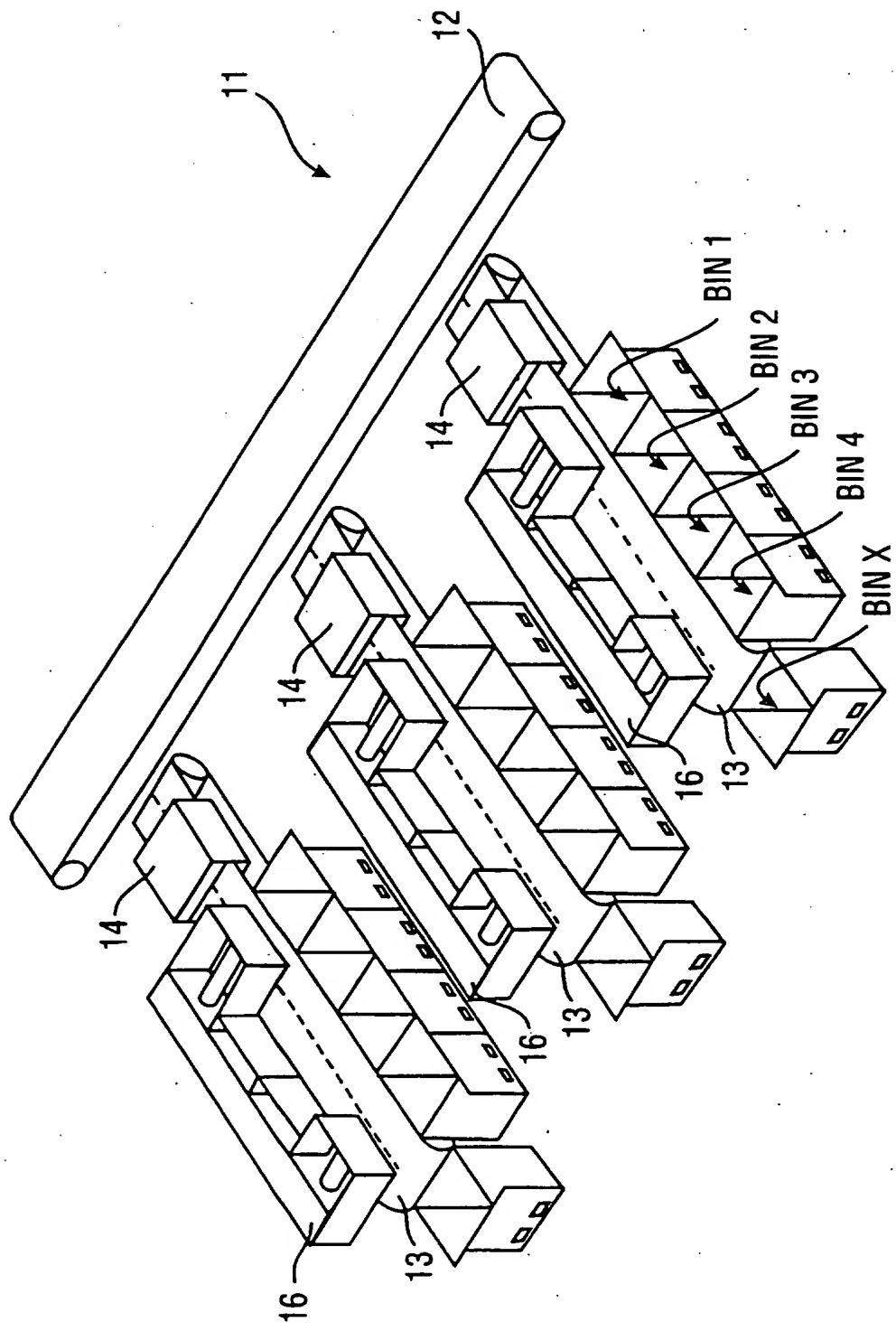


FIG. 1

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2/15

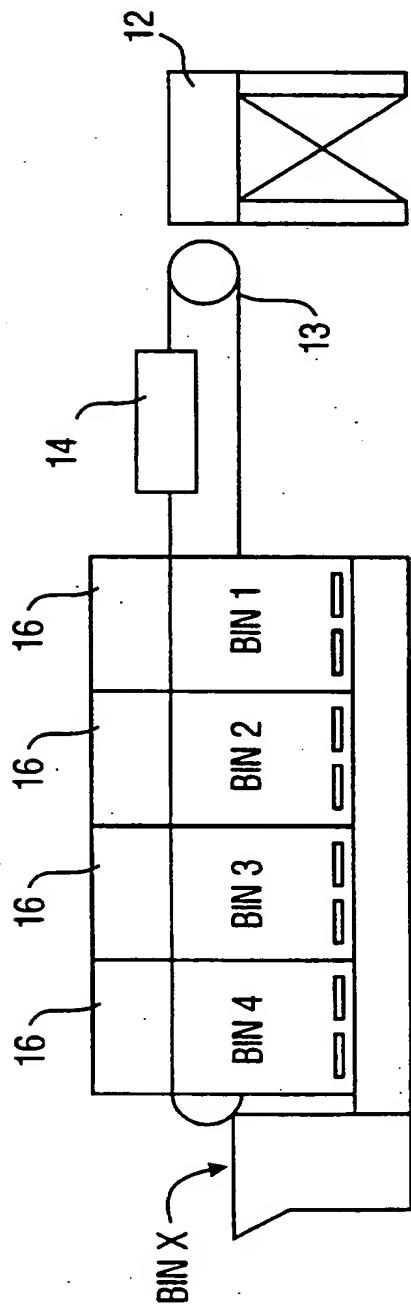


FIG. 2A

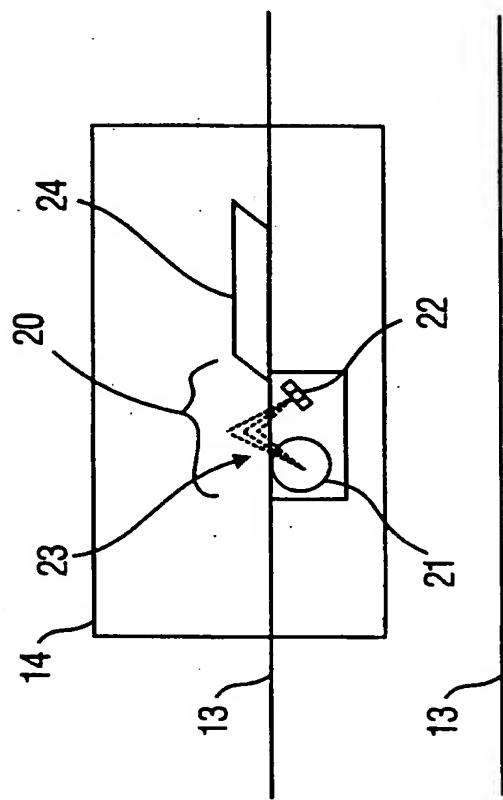


FIG. 2B

3/15

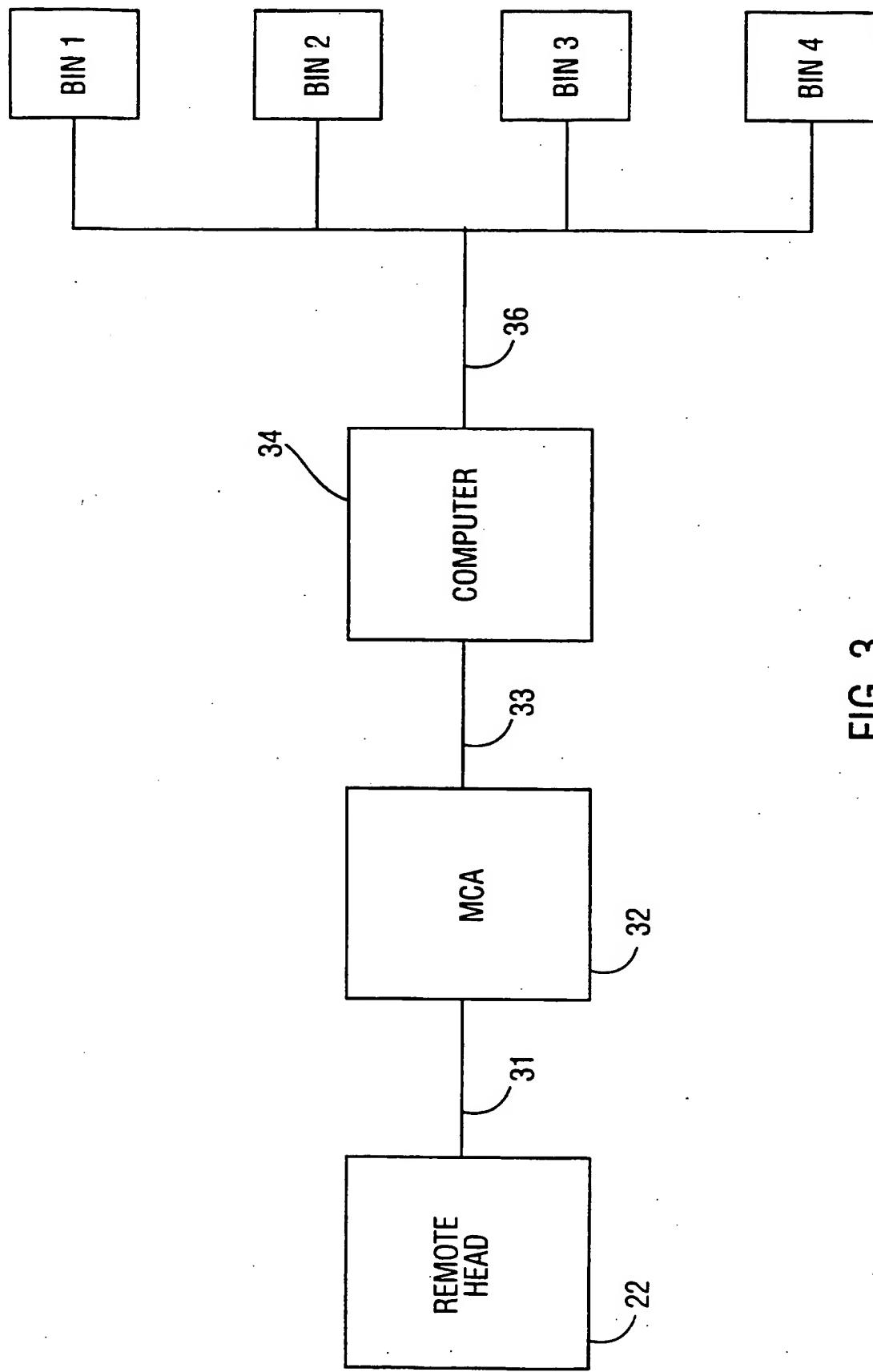


FIG. 3

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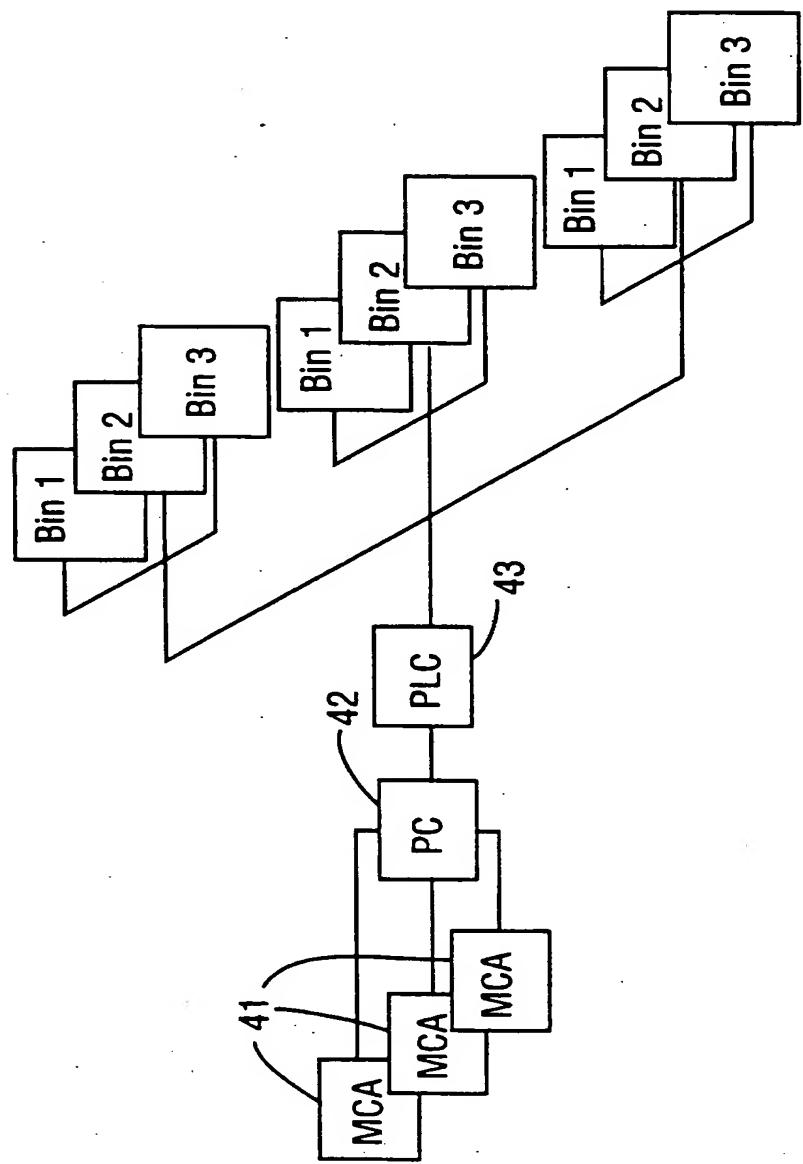


FIG. 4

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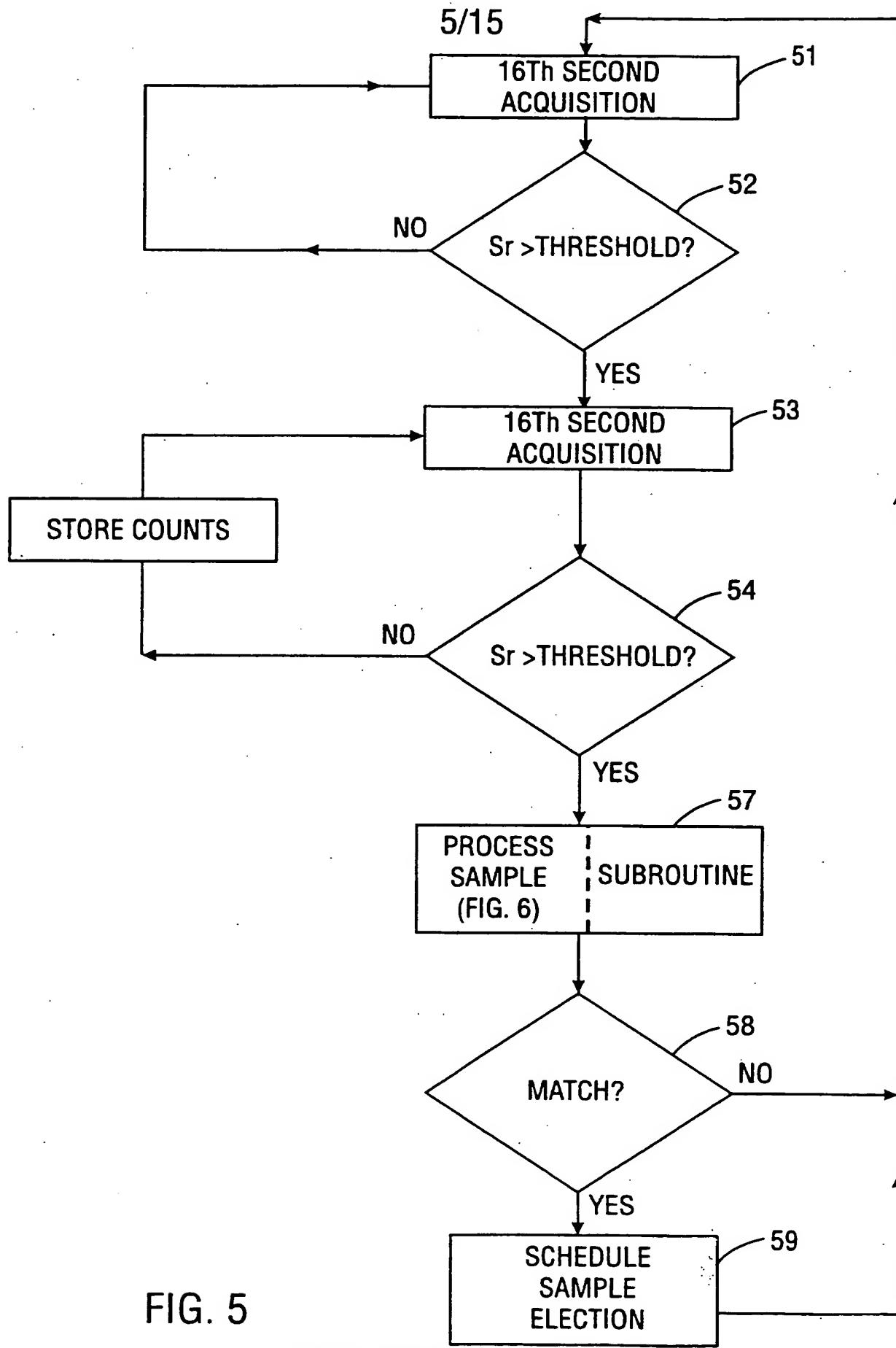
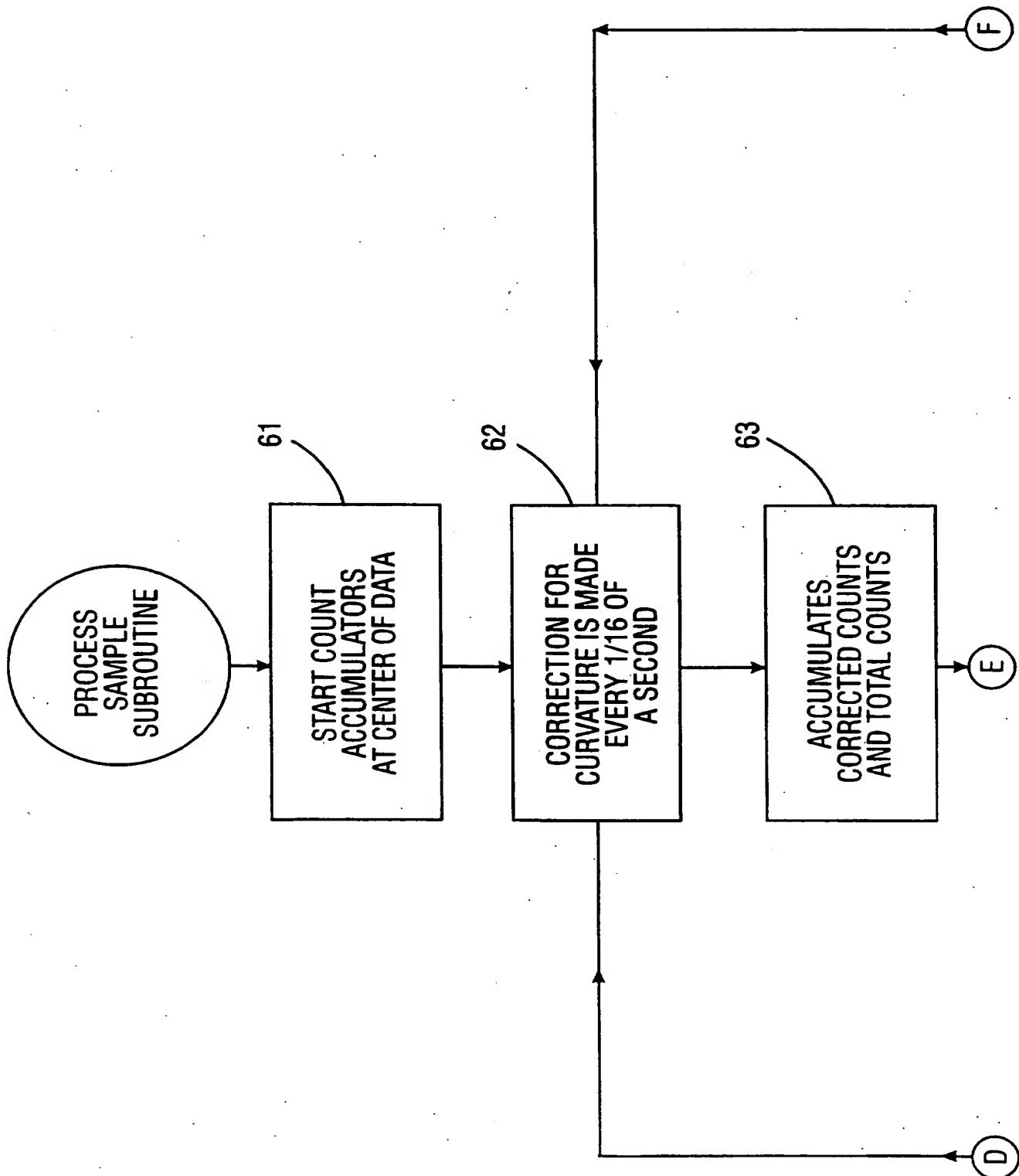


FIG. 5

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6/15

FIG. 6A



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7/15

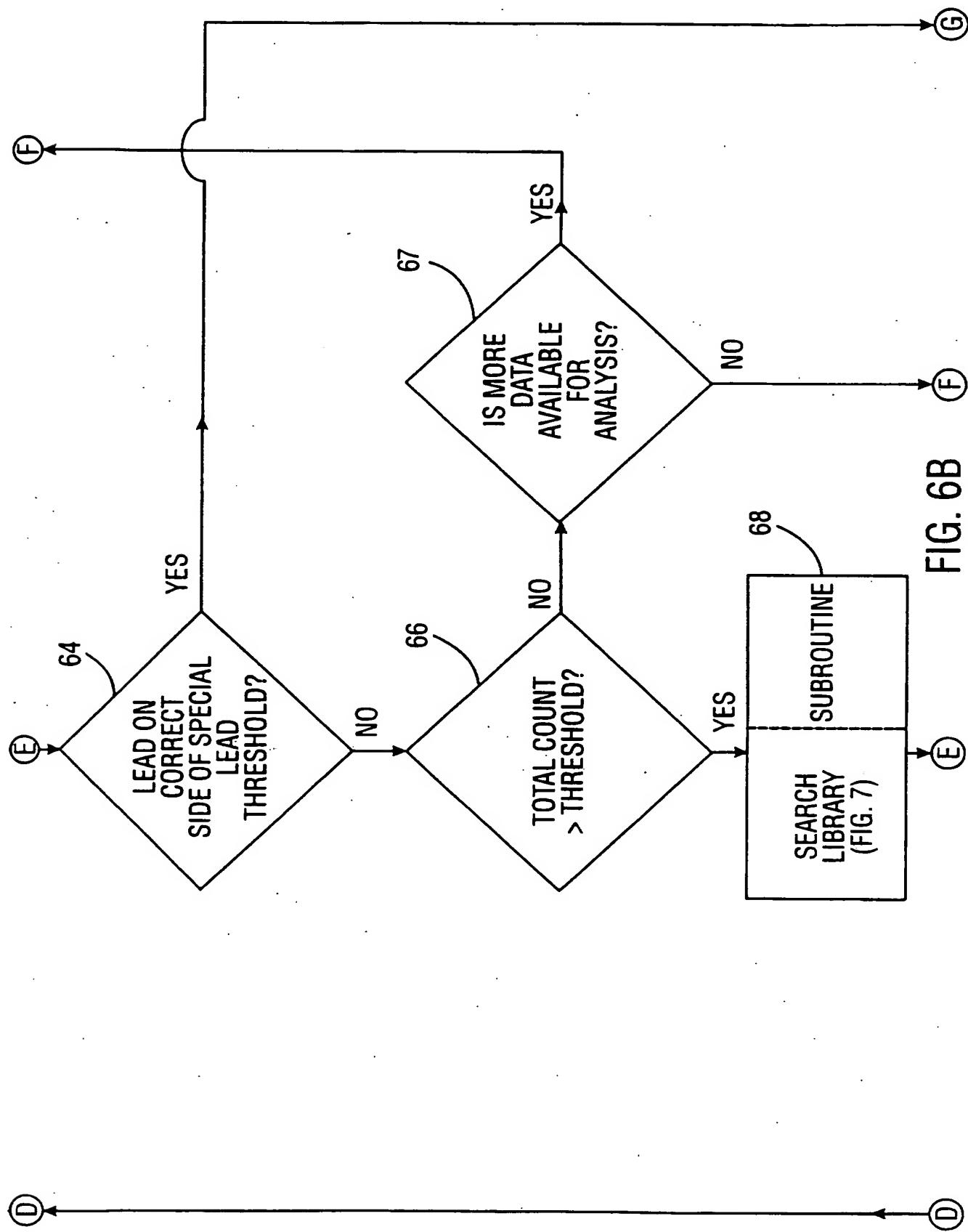


FIG. 6B

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8/15

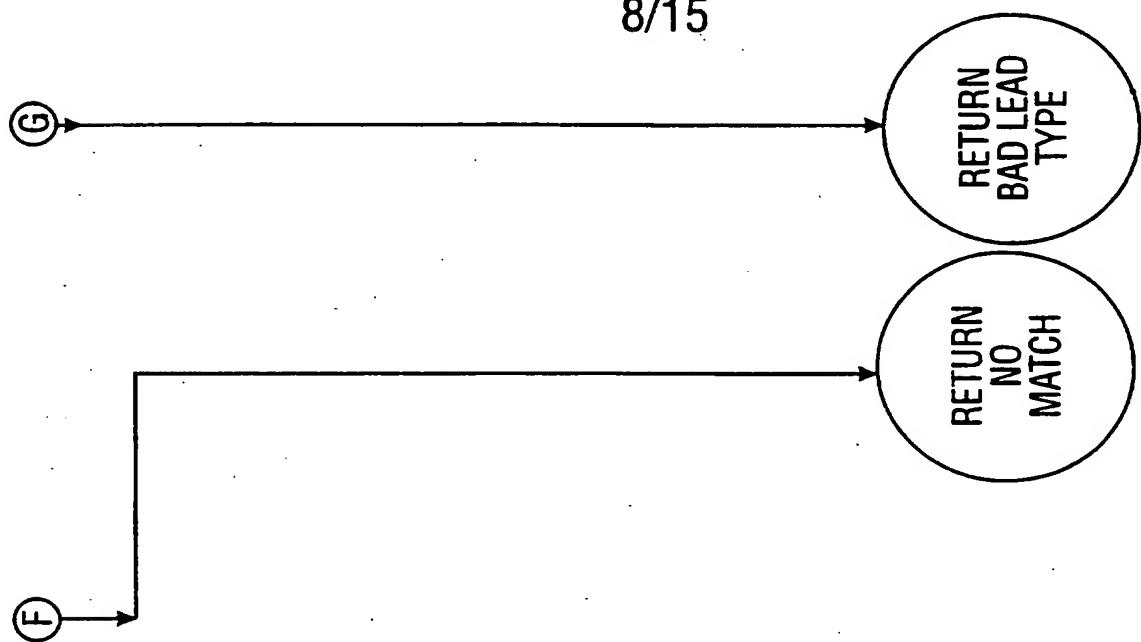
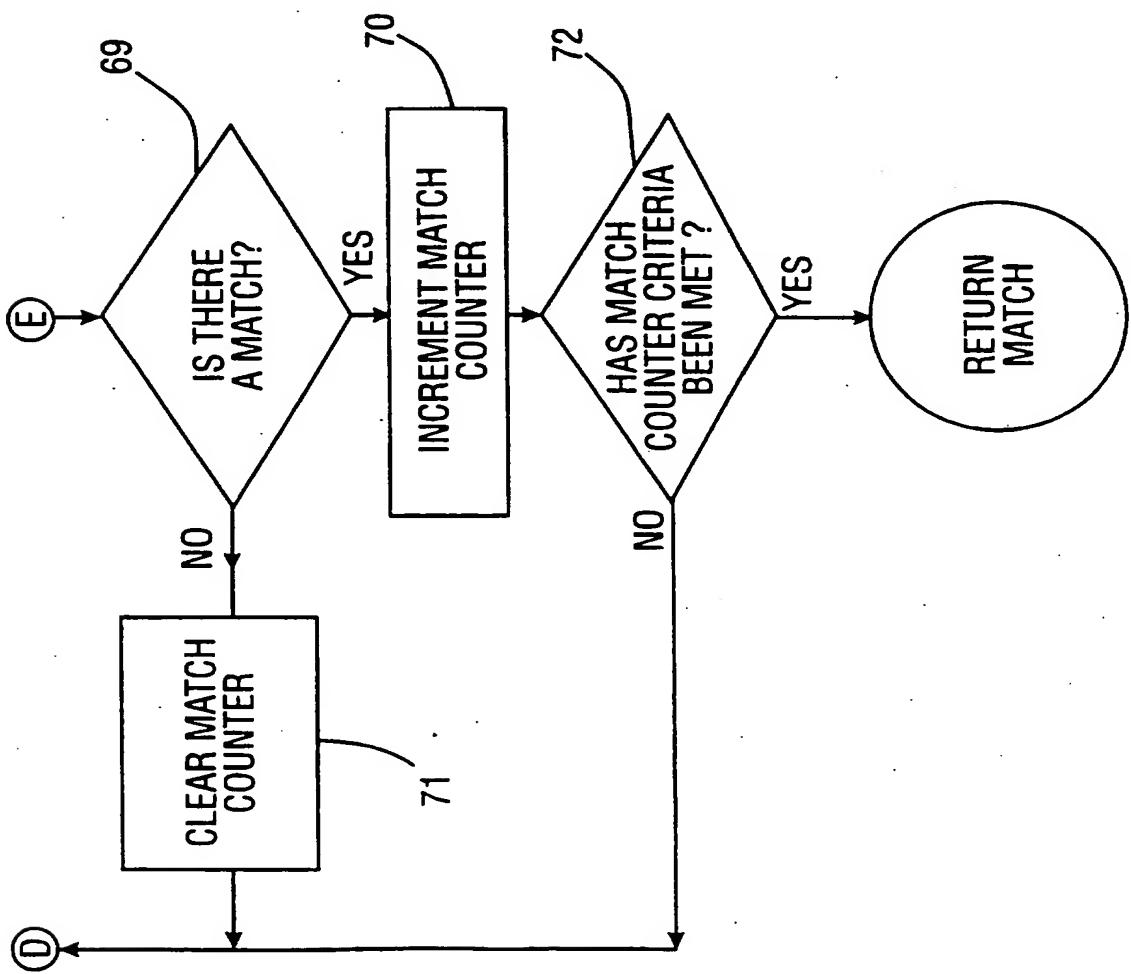


FIG. 6C



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9/15

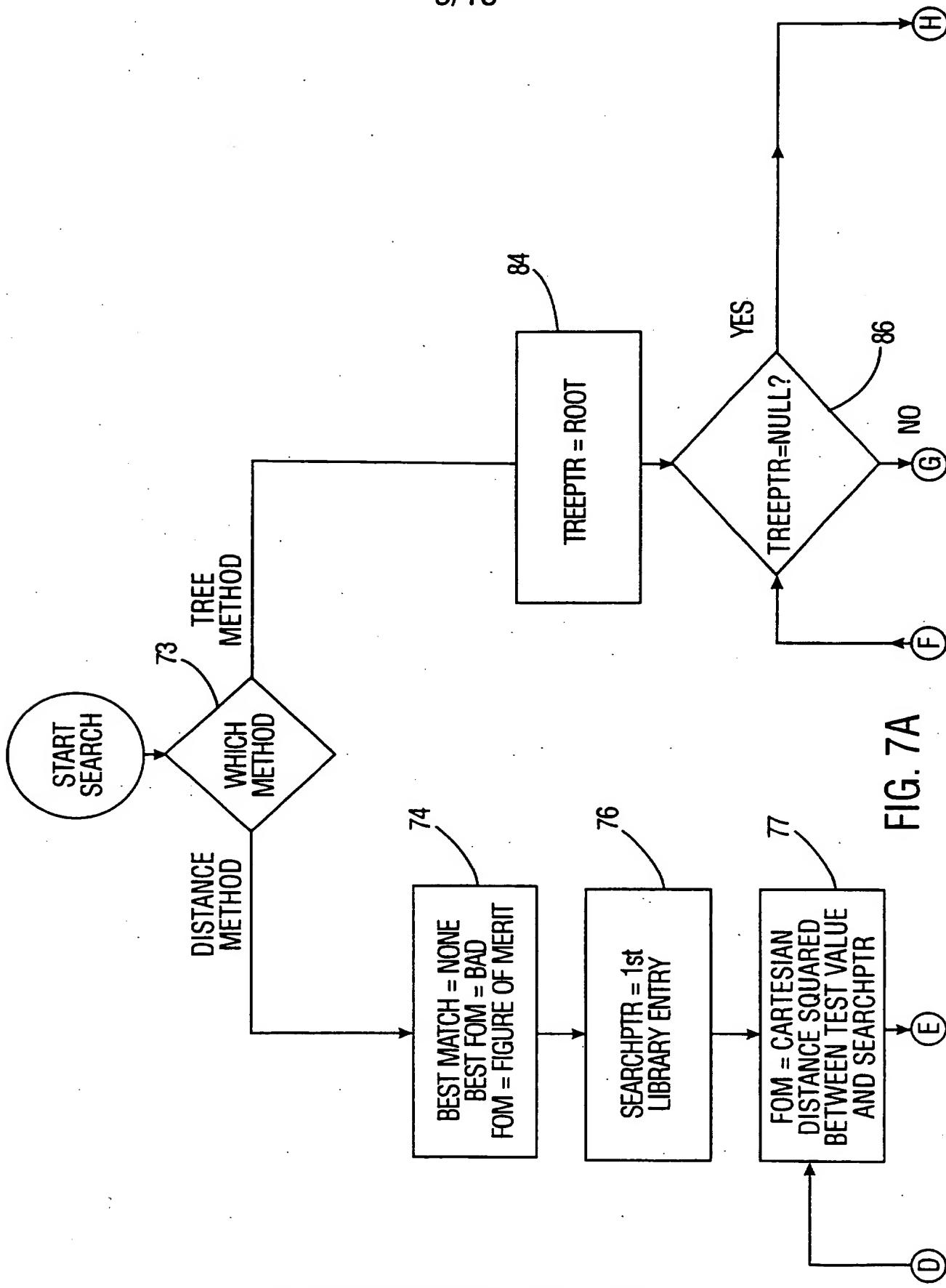


FIG. 7A

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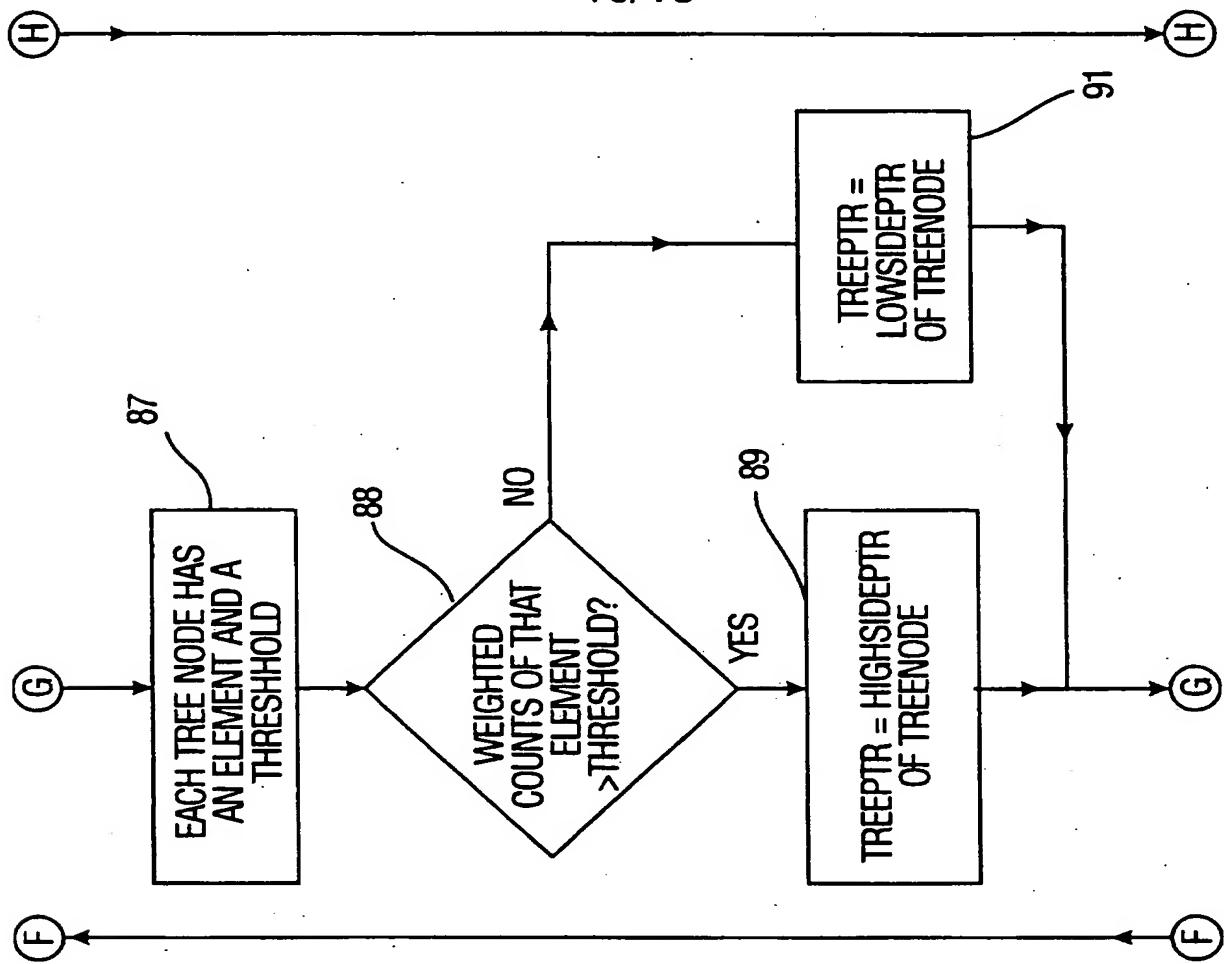
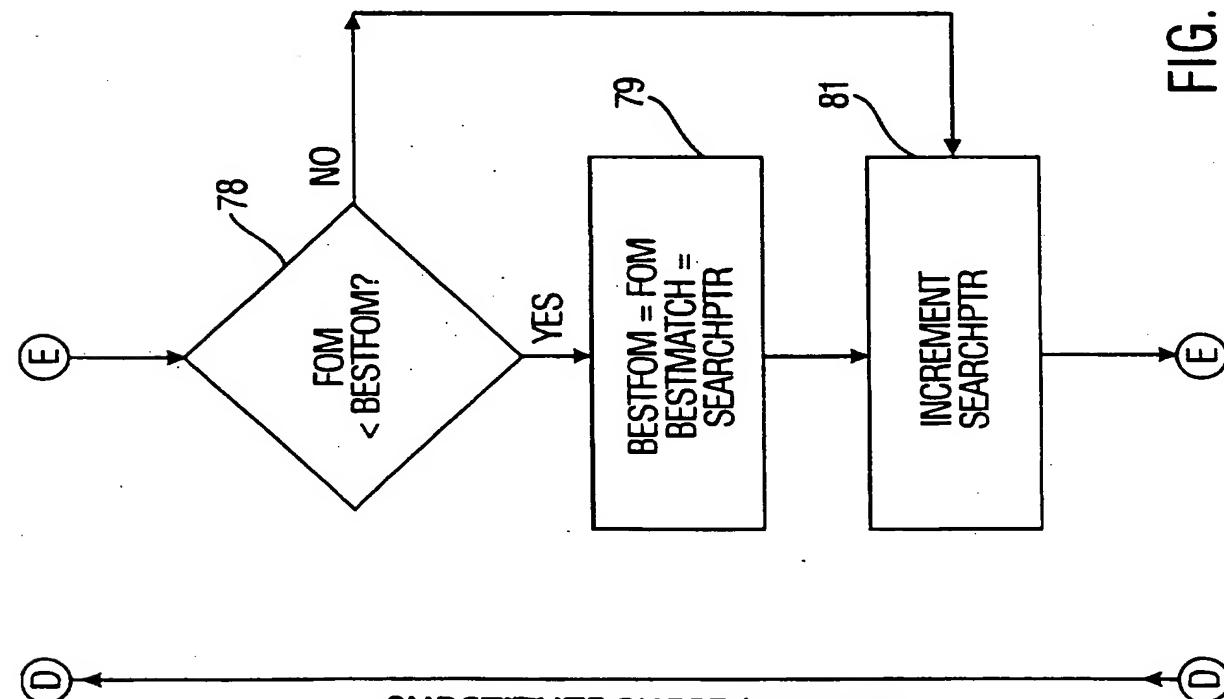


FIG. 7B



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11/15

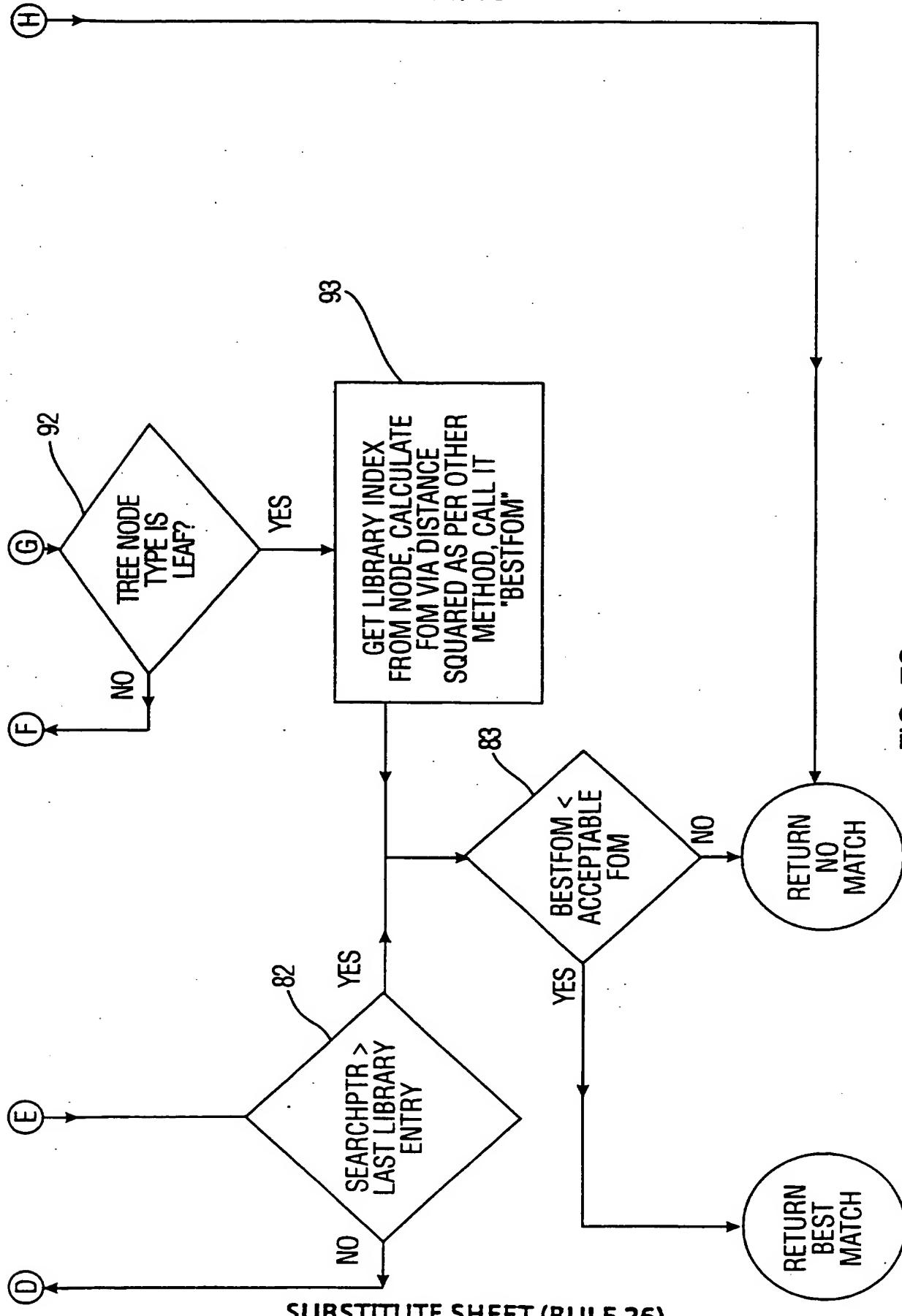


FIG. 7C

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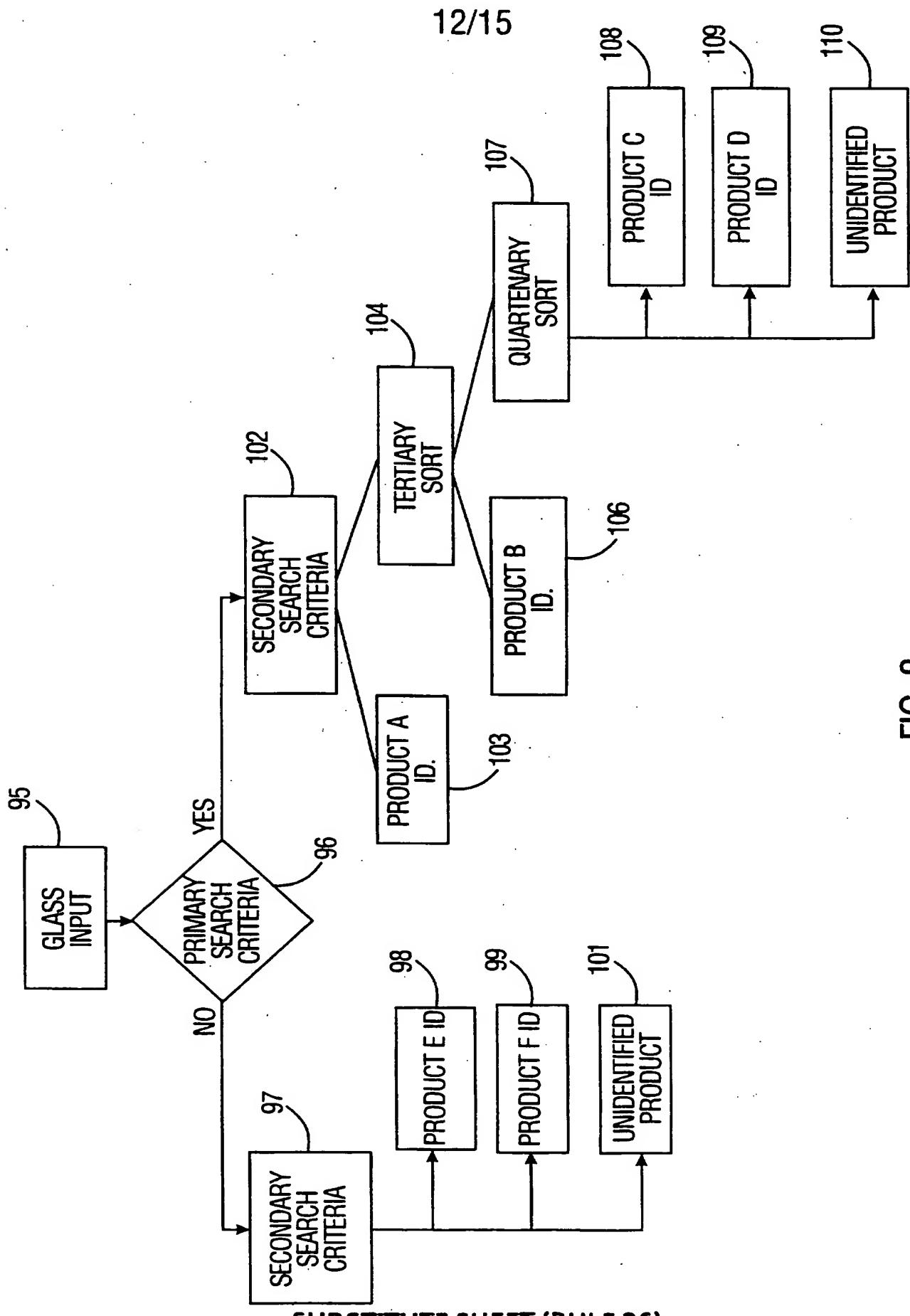


FIG. 8

13/15

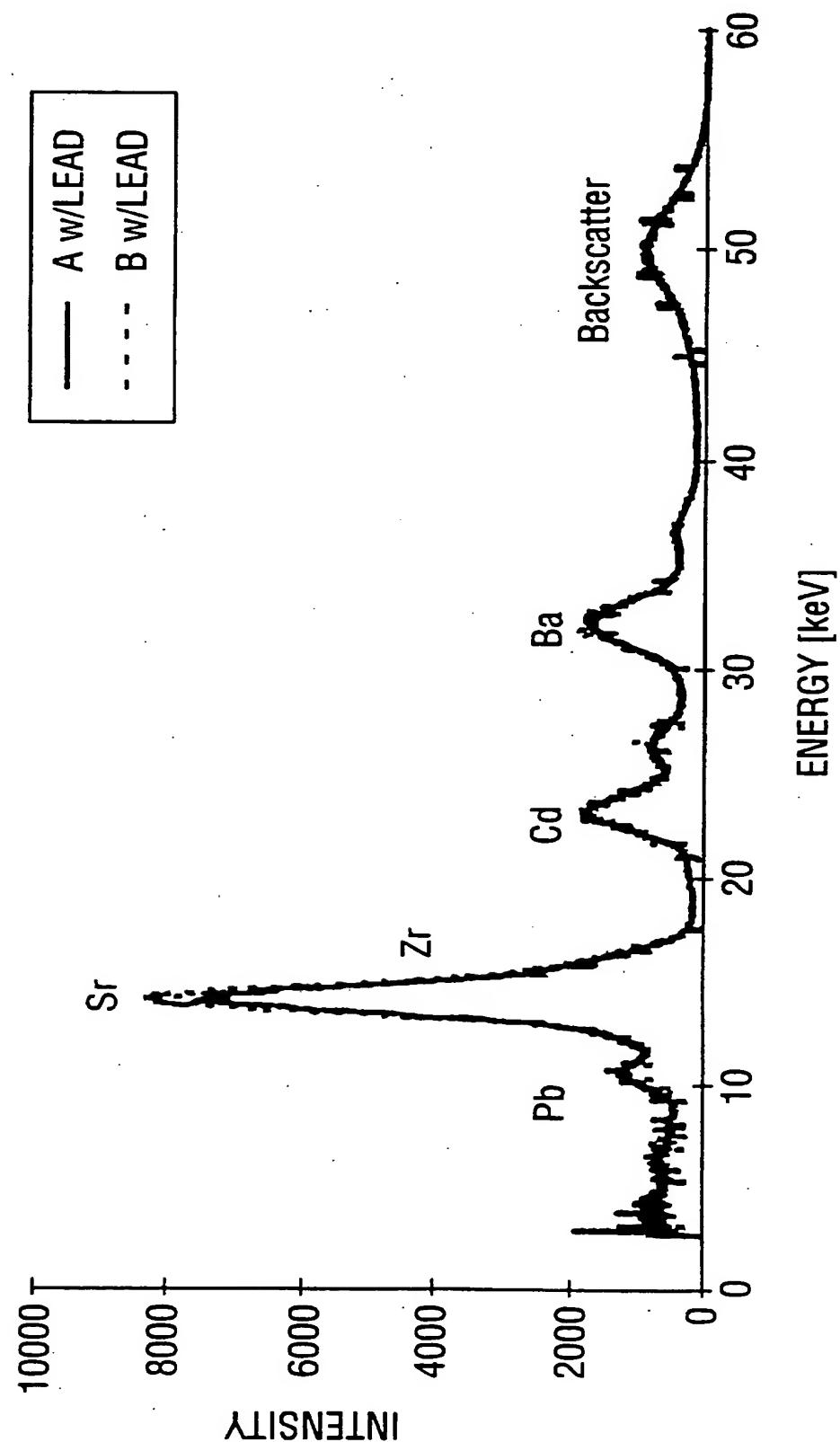


FIG. 9

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14/15

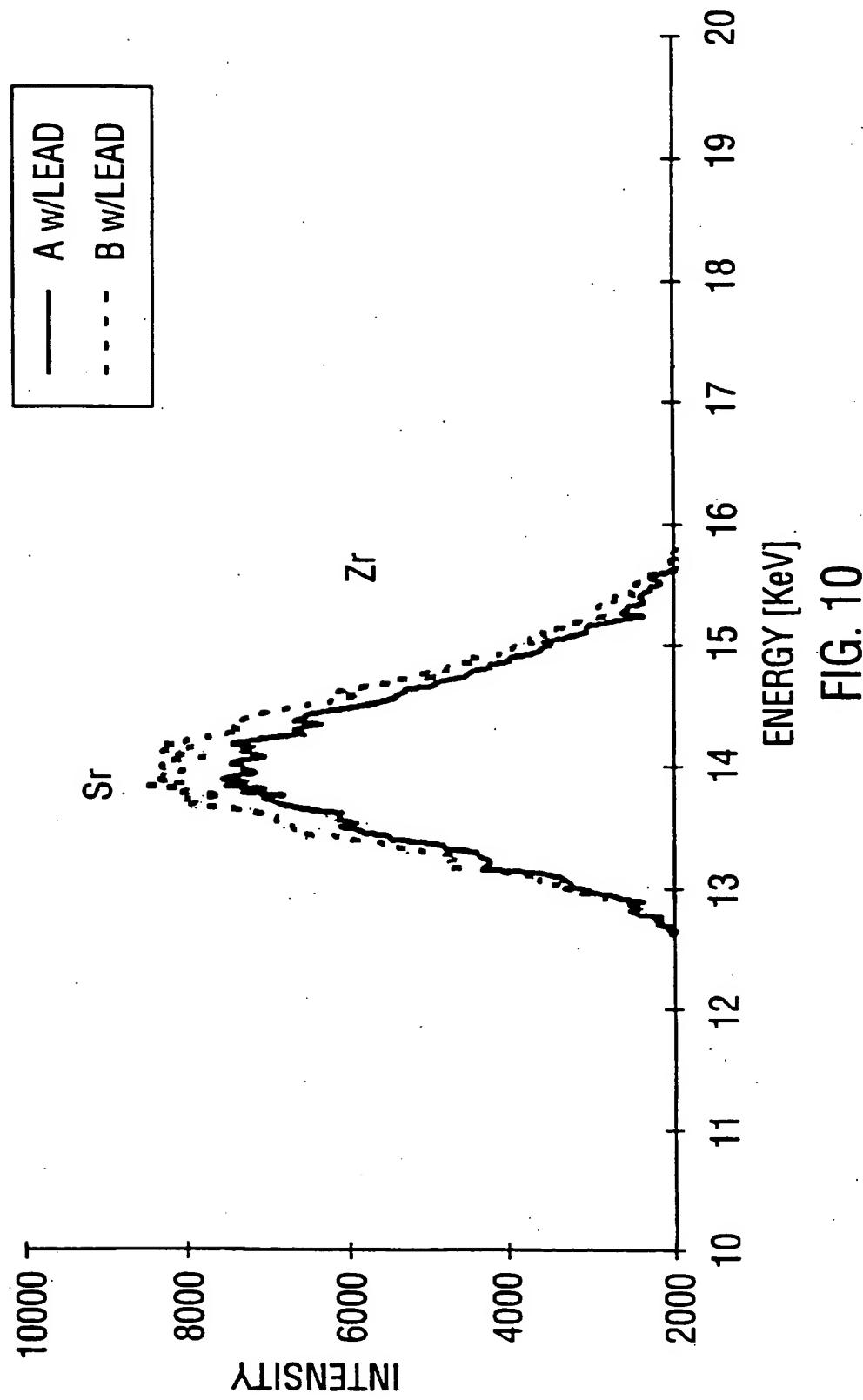
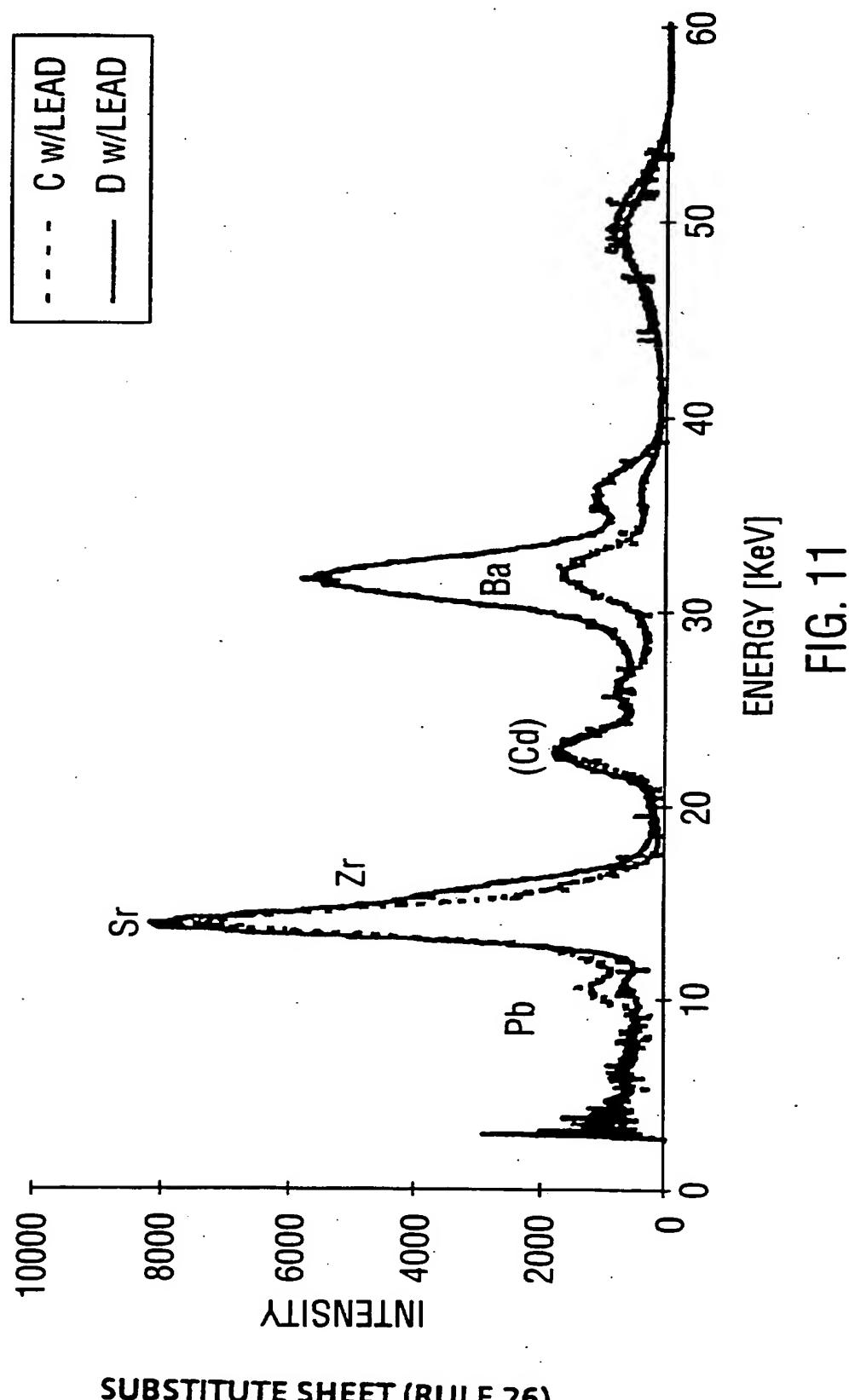


FIG. 10

15/15



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/00944

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : G01N 23/223

US CL : 378/45

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 378/44, 5,48

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB, A, 1,162,173 (IMAMURA ET AL) 20 August 1969, entire document.	1-14
A	US, A, 5,081,658 (IMAI ET AL) 14 January 1992.	

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*&*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

30 APRIL 1996

Date of mailing of the international search report

06 MAY 1996

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